Chapter II.

Water Quality Data Review and Assessment

An analysis of water quality data for representative stations in the Christina Watershed was conducted as part of the low-flow TMDL development. Data collected from 1980-1997 were examined, and the last 5 years of data (1993-1997) were used to represent existing conditions. Water quality data at the selected stations were combined with measured or estimated flow rate data in order to calculate mass loads and to identify data during low flow conditions. The analyses focused on water quality parameters related to organic and nutrient enrichment and included dissolved oxygen, pH, nitrogen, and phosphorus concentrations. The objectives of these analyses were to:

1. Describe existing water quality during low flow conditions;
2. Assess the occurrence of water quality criteria excursions; and
3. Identify any changes in low-flow water quality conditions over time.

The procedures and results of the data analyses are discussed individually for each stream.

Brandywine River

Two water quality datasets were reviewed for the Brandywine:

A. Continuous dissolved oxygen (DO) and pH data from USGS monitoring stations; and

B. Nutrient data collected by USGS, PA DEP, and DE DNREC monitoring programs.

The stations included in the datasets are listed in Table 1. Water quality measurements from each dataset were first combined with stream flow measurements from the USGS gaging stations. The analysis of the each dataset is discussed below.

Table 1. Stations and data availability for the low flow analyses.

Stream Reach	Gage Number	Location	Data Available
East Branch Brandywine	1480700	Above Downingtown	Nutrients, Flow
East Branch Brandywine	1480870	Below Downingtown	DO, pH, Nutrients, Flow
East Branch Brandywine	1480950	at Wawaset	Nutrients, Flow (estimated)
West Branch Brandywine	1480500	at Coatesville	Nutrients, Flow
West Branch Brandywine	1480617	at Modena	DO, pH, Nutrients, Flow
West Branch Brandywine	1480640	at Wawaset	Nutrients, Flow (estimated)
Mainstem Brandywine	1481000	at Chadds Ford	DO, pH, Nutrients, Flow
Mainstem Brandywine	1481500	Wilmington	Nutrients, Flow

Analysis of Continuous DO and pH Data

Continuous DO, pH, and flow rate data were available at the station below Downingtown on the East Branch Brandywine, at Modena on the West Branch Brandywine, and at Chadds Ford on the mainstem Brandywine River. The data from the **July-September** periods for each year from 1980-1997 were selected for analysis since this period is typically representative of critical low-flow water quality conditions. The analyses included a frequency analysis of water quality criteria excursions for July-September of each year, a frequency analysis of flow rates during water quality criteria excursions, and the identification of any changes or trends in DO or pH during low-flow conditions.

Frequency Analysis of DO and pH Criteria Excursions and Flow Rates

The continuous DO and pH data collected during July-September of each year were compared to the applicable water quality criteria for DO and pH to determine the frequency of excursions. The PA DEP water quality criteria for these stations include an average daily DO of 5.0 mg/L, minimum DO of 4.0 mg/L, and pH between 6 and 9. The DRBC water quality criteria at these stations are the same as PA DEP's for DO, however the DRBC maximum pH is 8.5 (compared to 9.0 for PA DEP). Although there is no water quality standard for the daily range in DO (Maximum DO- Minimum DO), the largest daily DO range observed for each year and the number of days with DO ranges above 6.0 mg/L were tabulated as an indication of photosynthetic activity.

Violations of the DO and pH criteria were observed at the gages on the East and West Branches as summarized in Tables 2 and 3. Minimum and average DO criteria excursions were observed on the East and West Branches through 1987, however no DO criteria excursions occurred on these branches since that time. The abrupt improvement in DO suggests that organic wasteloads were reduced to these streams during 1988, and these changes may have been brought about by improvements in wastewater treatment practices.

Violations of the maximum pH standard (pH <= 8.5 for DRBC and pH <= 9 for PA DEP) were recorded over the entire period of record on the West Branch Brandywine, and from 1988-1997 for the East Branch Brandywine. Figures 1-2 show the correlation between the maximum pH versus the maximum daily DO range observed for the East Branch (1989-1997) and West Branch (1981-1997) of the Brandywine. The correlation between DO range and maximum pH is likely caused by the uptake of carbon dioxide and nutrients during photosynthesis which in turn effects the pH and alkalinity of the stream water (Stumm and Morgan, 1997).

Only two violations of the minimum DO standard were observed at the Chadds Ford gage on the mainstem river from 1980-1997 for the July-September data set (Table 4). There were excursions of the DRBC maximum pH criteria throughout the period of record.

Reserved for Table 2 – DO-ph excursions East Br Brandy

Table 2. Summary of DO and pH Criteria Excursions for the July-September Data on the East Branch Brandywine River Below Downingtown.

Year	No. of Days Exceeding Mean Daily DO <5.0 mgl	No. of Days Exceeding Minimum DO < 4.0 mg/L	No. of Days Exceeding DO Range > 6.0 mg/L	No. of Days Exceeding Maximum pH >8.5	Maximum DO Range	Maximum pH
1980	0	3	9	0	8.5	8.3
1981	37	67	27	0	9.3	7.9
1982	0	1	0	0	3.9	8.0
1983	3	3	0	0	5.7	7.7
1984	7	8	2	0	9.7	8.0
1985	23	48	14	0	8.6	8.0
1986	4	6	2	0	6.4	8.5
1987	4	9	22	13	9.5	8.9
1988	0	0	10	12	8.6	9.0
1989	0	0	0	0	4.2	8.3
1990	0	0	0	8	5.8	8.7
1991	0	0	10	15	7.4	8.9
1992	0	0	32	44	9.6	9.4
1993	0	0	23	47	10.1	9.3
1994	0	0	17	54	9.0	9.2
1995	0	0	6	12	8.7	8.9
1996	0	0	0	0	4.6	8.4
1997	0	0	7	27	7.6	9.3

Reserved for Table 3 DO ph excur West Branch

Table 3. Summary of DO and pH Criteria Excursions for the July-September Data on the West Branch Brandywine River at Modena.

Year	No. of Days Exceeding Mean Daily DO <5.0 mg/L	No. of Days Exceeding Minimum DO < 4.0 mg/L	No. of Days Exceeding DO Range > 6.0 mg/L	No. of Days Exceeding Maximum pH >8.5	Maximum DO Range	Maximum pH
1981	2	12	11	1	7.7	8.7
1982	0	1	0	0	5.8	8.4
1983	0	35	27	44	10.1	9.1
1984	0	0	0	6	4.8	8.6
1985	4	47	20	2	9.2	8.9
1986	0	6	0	32	7.6	8.9
1987	0	12	23	35	8.6	9.1
1988	0	0	23	66	10.6	9.5
1989	0	0	5	39	10.6	9.5
1990	0	0	38	52	12.8	9.6
1991	0	0	50	55	12.8	9.5
1992	0	0	29	27	9.3	9.2
1993	0	0	6	59	6.6	9.2
1994	0	0	3	50	6.3	9.1
1995	0	0	0	3	5	8.7
1996	0	0	0	4	3.7	8.7
1997	0	0	0	56	4.2	9.1

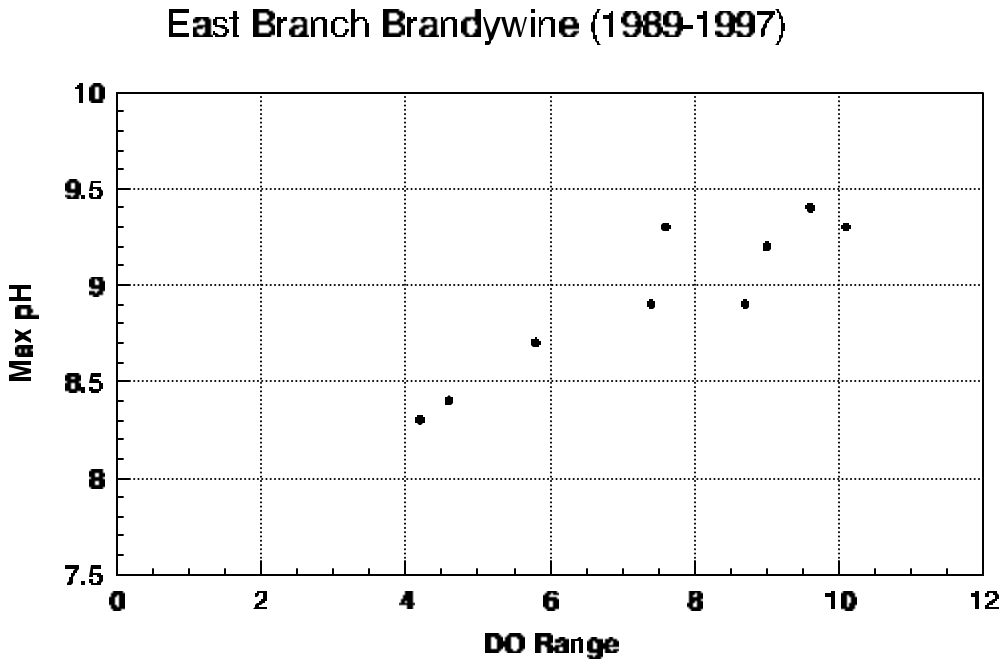


Figure 1. Correlation between maximum daily pH and maximum DO range for 1989-1997 on the East Branch Brandywine River.

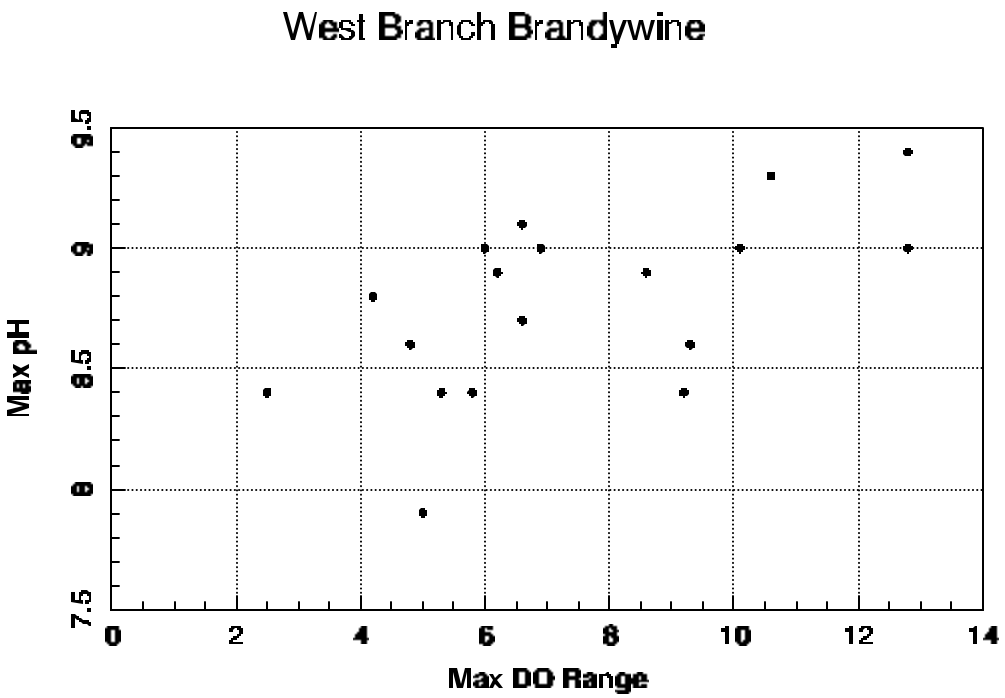


Figure 2. Correlation between maximum daily pH and maximum DO range for 1981-1997 on the West Branch Brandywine River.

Reserved for Table 4 Chadds Ford Do –ph

Table 4. Summary of DO and pH Criteria Excursions for the July-September Data on the Mainstem Brandywine River at Chadds Ford.

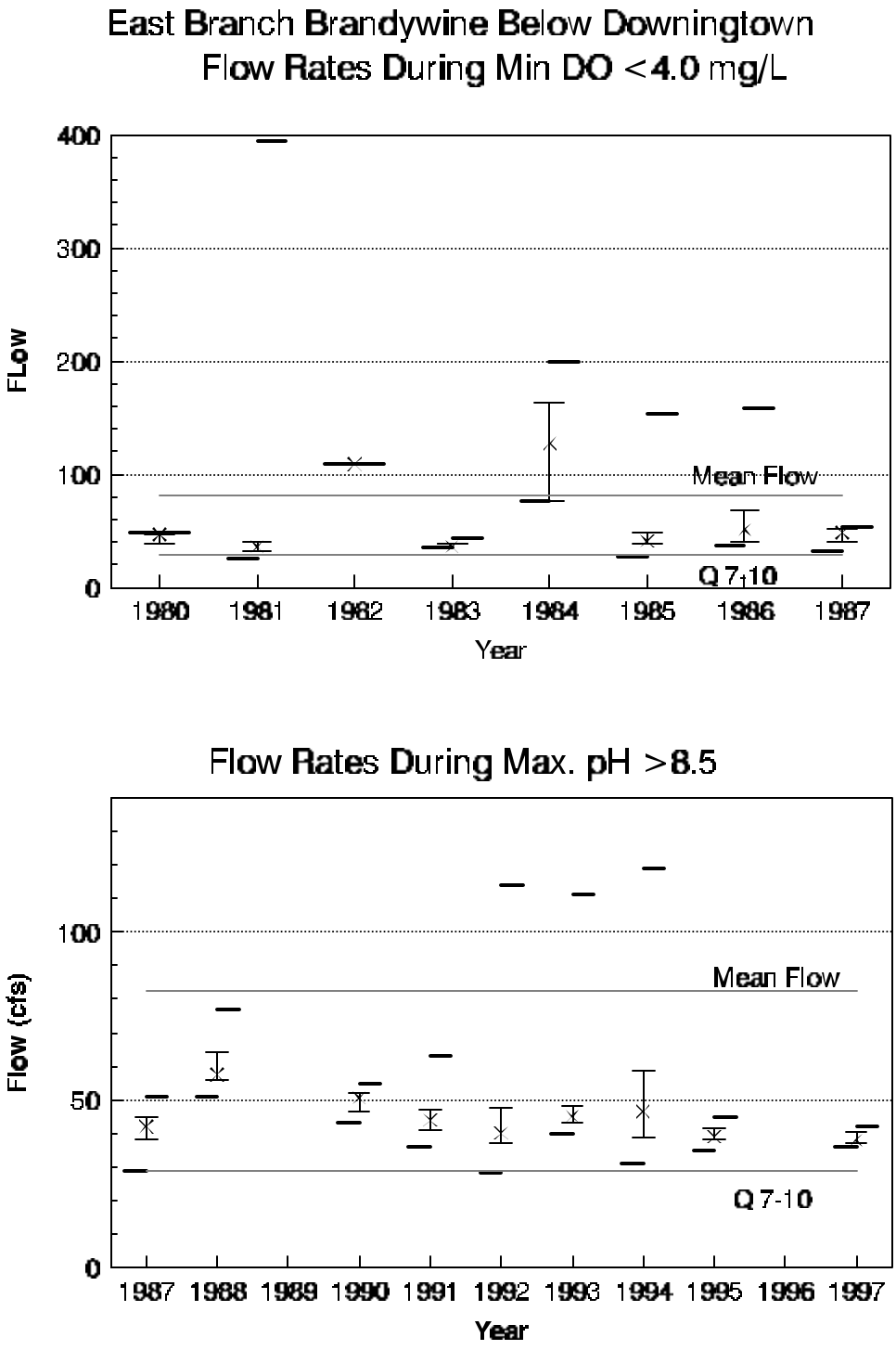
Year	No. of Days Exceeding Mean Daily DO <5.0 mg/L	No. of Days Exceeding Minimum DO < 4.0 mg/L	No. of Days Exceeding DO Range > 6.0 mg/L	No. of Days Exceeding Maximum pH >8.5	Maximum DO Range	Maximum pH
1980	0	0	0	0	4.7	8.5
1981	0	0	0	1	5.7	8.6
1982	0	0	0	0	4.4	8.3
1983	0	0	0	6	5.3	8.8
1984	0	1	0	0	4.3	8.5
1985	0	0	0	4	4.1	8.7
1986	0	0	0	0	3.3	8.4
1987	0	0	0	7	4.2	8.9
1988	0	0	0	3	3.8	8.8
1989	0	0	0	0	2.9	8.6
1990	0	0	0	1	3.3	8.7
1991	0	0	0	2	3.7	8.6
1992	0	0	0	2	4.1	8.7
1993	0	0	0	0	3.4	8.4
1994	0	0	0	4	3.1	8.7
1995	0	1	0	0	5.6	8.0
1996	0	0	0	0	3.2	8.3
1997	0	0	2	7	7.1	8.7

Box plots of the distribution of flow rates occurring during the DO and pH criteria excursions for the East and West Branch Brandywine River are shown in Figures 3-4. Each graph also shows the Q7-10 and the harmonic mean flow rate for each station (USGS). The flow rates occurring during the criteria excursions are predominantly lower than the harmonic mean flow rate, but greater than the Q7-10 critical flow. Two significant findings can be drawn from these observations:

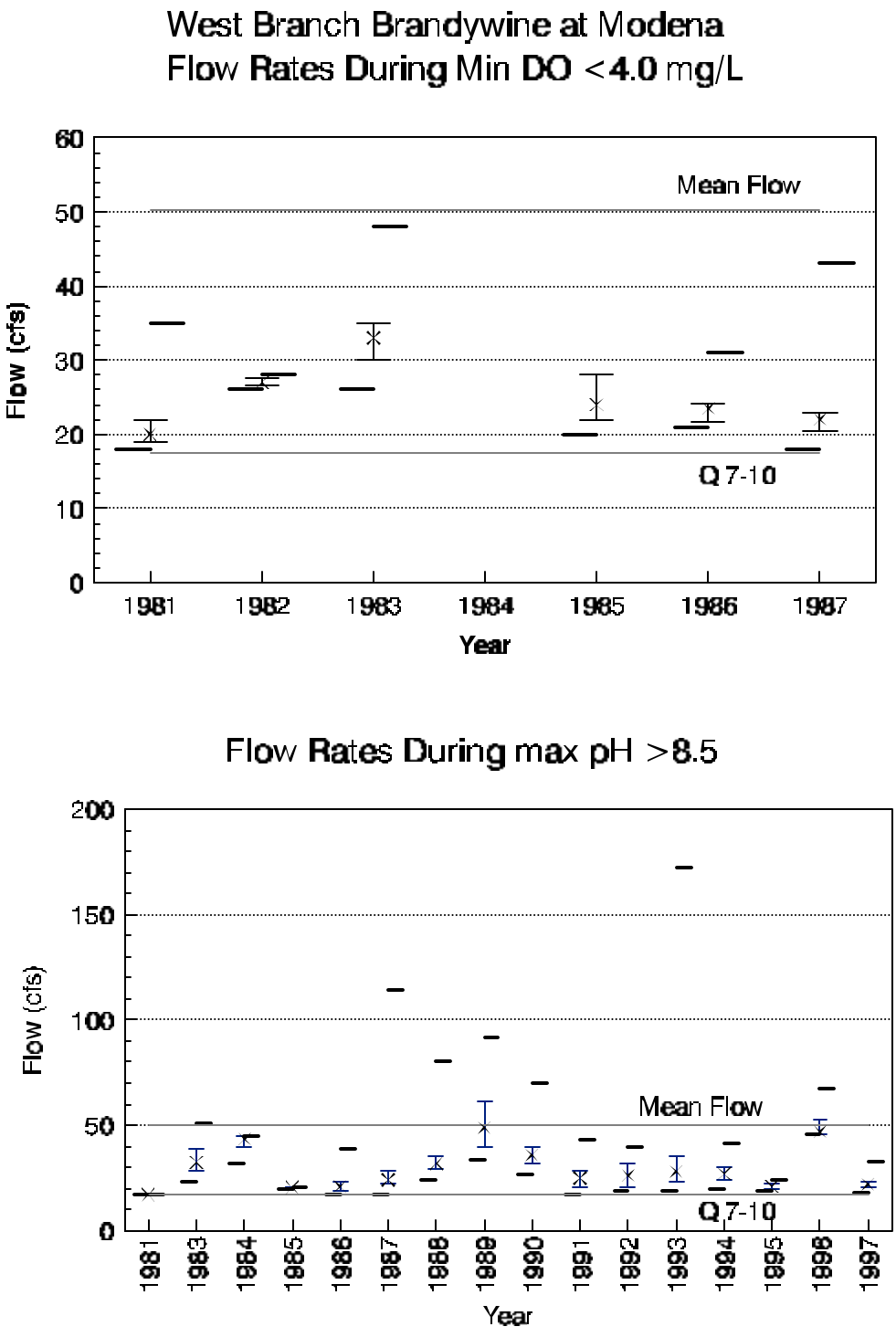
1. low flow rates are the most critical conditions for meeting the DO and pH criteria for these streams; and
2. the observed criteria excursions are violations of the water quality standards, which apply to criteria excursions only when the flow rate is equal to or greater than the Q7-10.

The occurrence of high DO levels with high flow rates is also evident in Figures 5 and 6, which show the time series plots of the July daily minimum DO concentrations and flow rates (shown as log flow) at the Modena station on the West Branch Brandywine and below Downingtown on the East Branch Brandywine, respectively. Several important observations can be made from these graphs:

1. There are several years of relatively high flow rates including 1984, 1988-1990, and 1996. During these periods, the DO levels tend to be high.
2. There was a major increase in DO levels for both streams occurring 1988-1989. Although this period also corresponds to a period of higher flow rates, it is likely the increase in DO is due to a decrease in wasteloads entering each stream since the DO levels remain high after the period of high flow rates.



Figures 3a and 3b. Distribution of flow rates during excursions of DO and pH criteria for the East Branch Brandywine River.



Figures 4a and 4b. Distribution of flow rates during excursions of DO and pH criteria for the West Branch Brandywine River.

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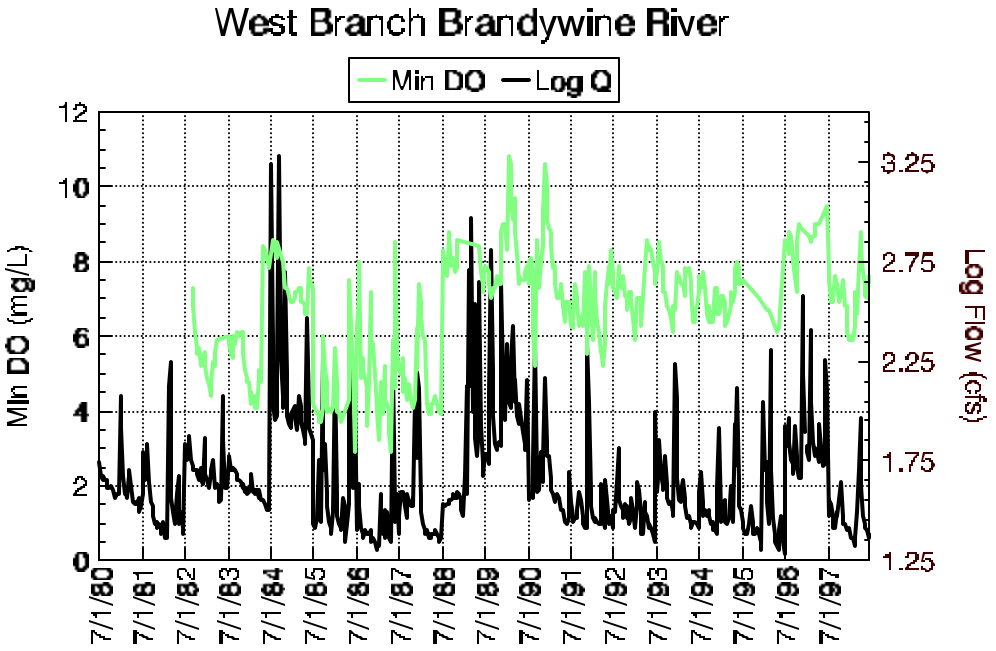

Figure 5. Minimum DO and Flow Rate for July Time Series at Modena, West Branch Brandywine River.

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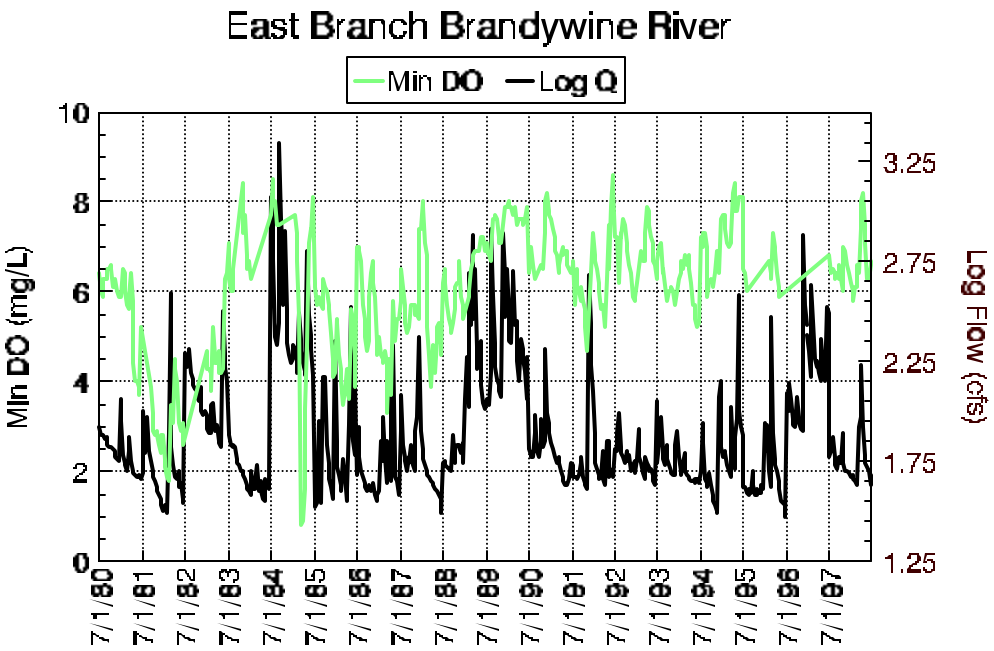

Figure 6. Minimum DO and Flow Rate for July Time Series below Downingtown, East Branch Brandywine River.

Change/Trend Analyses of Continuous DO and pH Data

The continuous DO and pH data collected during July through September were sorted by flow rate to identify low flow conditions. All data for stream flows less than the annual **10th percentile flow** were selected to represent low flow conditions for the change or trend analysis. Appendix A contains annual and July-September cumulative frequency distributions of stream flow rates at each gage. The annual 10th percentile flow corresponded to the 25th percentile flow for the July-September data at each gage. The July-September low flow data set was then summarized for each year to determine the median, maximum, minimum, 25th percentile, and 75th percentile parameter values for each year. These values were then used to develop box plots to illustrate the changes in each parameter over time. A Mann-Whitney nonparametric statistical test was run to identify any statistically significant changes in the median parameter values over the selected time periods. The significant findings for each station are presented below.

East Branch Brandywine below Downingtown :

- Annual 10th percentile flow = 41 cfs, (25% flow for July-September);
- Step increases in minimum DO of 2.2 mg/L (Fig.7), mean DO of 2.4 mg/L (Fig.8), and % Saturation of Mean DO of 25 % (Fig. 9.) from 1980-1987 vs. 1990-1997.

- Step increase in mean daily pH of 0.8 (Fig. 10) and maximum pH of 1.2 (Fig. 11) from 1980-1987 vs. 1990-1997.

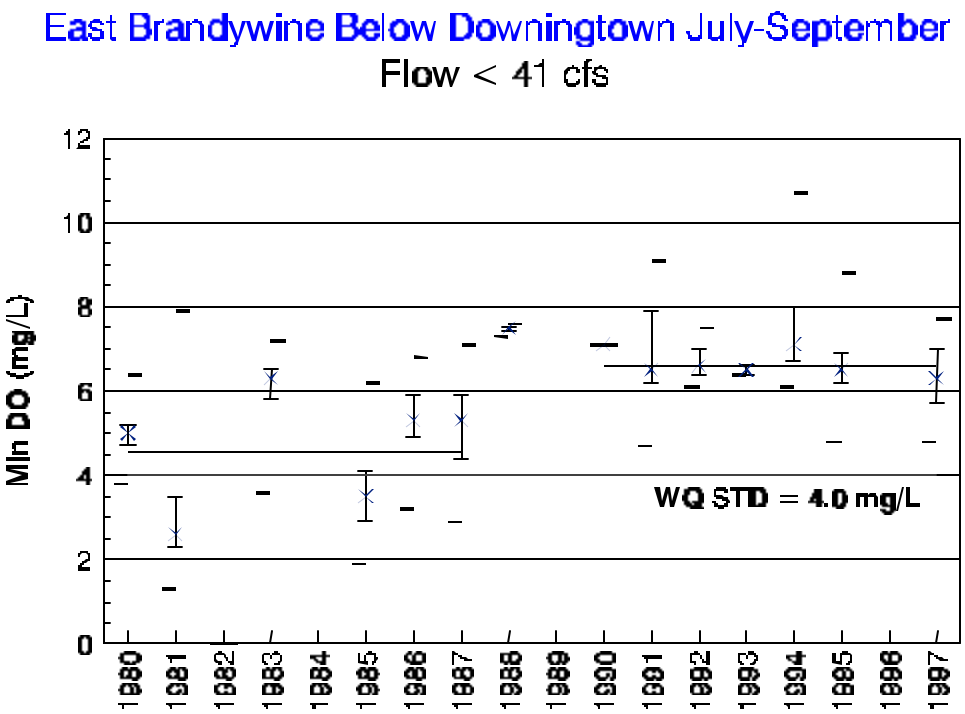

Figure 7. Box plots of minimum DO for the East Branch Brandywine below Downingtown for data from July-September at flows less than 41 cfs.

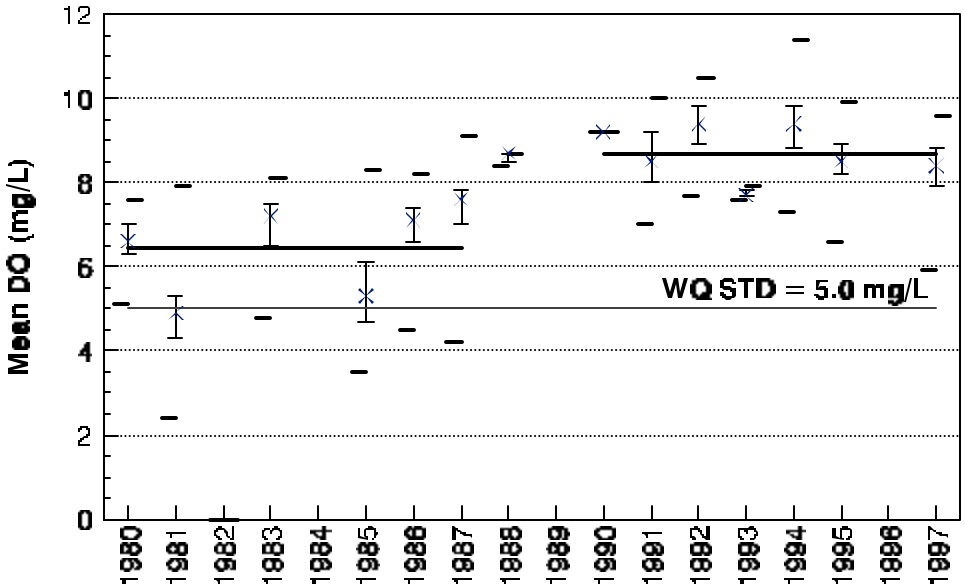

Figure 8. Box plots of mean DO for the East Branch Brandywine below Downingtown for data from July-September at flows less than 41 cfs.

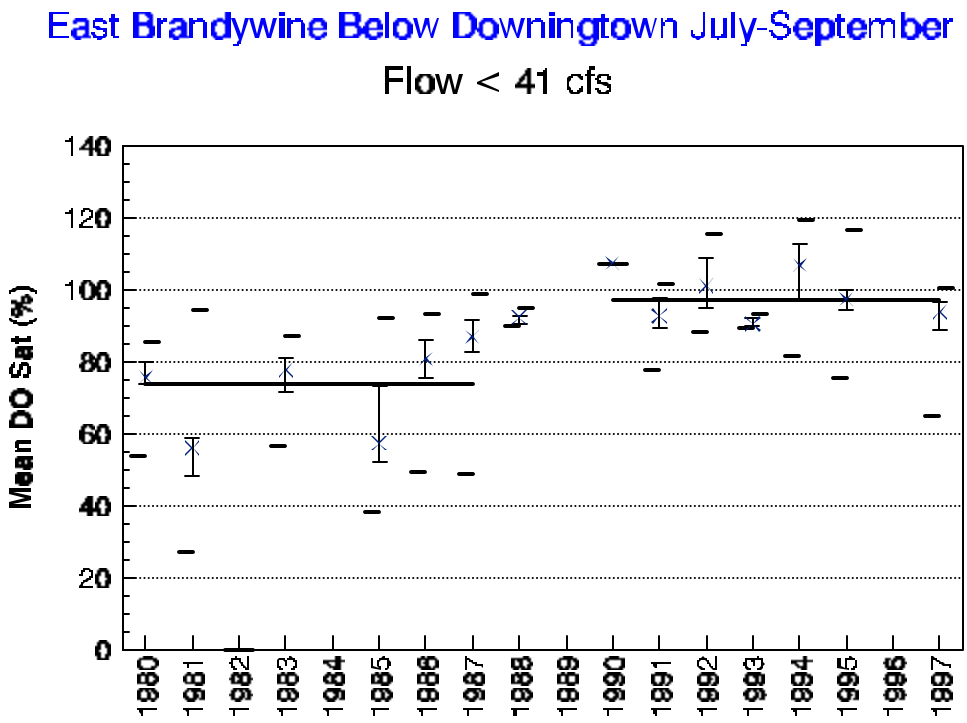

Figure 9. Box plots of mean DO % Saturation for the East Branch Brandywine below Downingtown for data from July-September at flows less than 41 cfs.

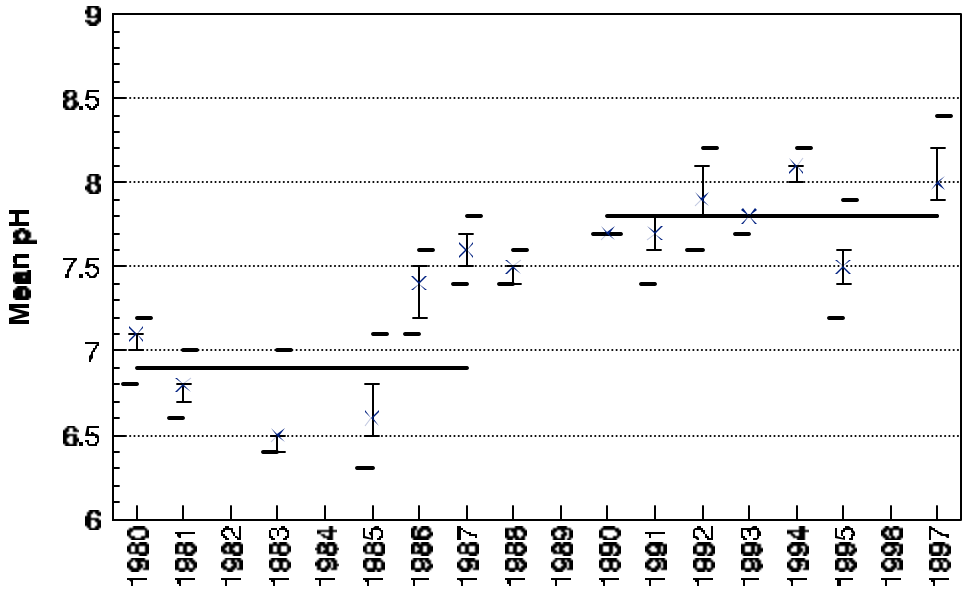

Figure 10. Box plots of mean pH for the East Branch Brandywine below Downingtown for data from July-September at flows less than 41 cfs.

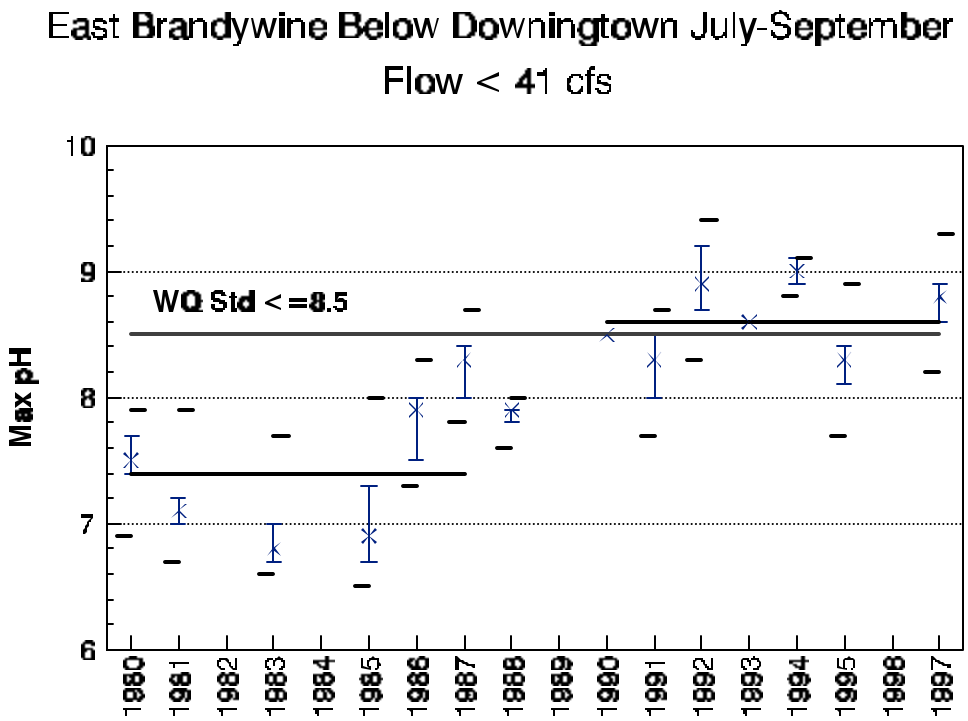

Figure 11. Box plots of maximum pH for the East Branch Brandywine below Downingtown for data from July-September at flows less than 41 cfs.

West Branch Brandywine at Modena :

- Annual 10th percentile flow = 25 cfs (25% flow for July-September);
- Step increases in minimum DO of 2.9 mg/L (Fig. 12), mean DO of 1.7 mg/L (Fig. 13), and mean DO % saturation of 21.4 % (Fig. 14) from 1980-87 vs 1991-1997.
- Step decrease in DO range of 2.5 mg/L (Fig. 15) from 1980-87 vs. 1995-97. The data from 1991-1994 suggests a period of transition.

- Step increase in maximum pH of 0.2 (Fig. 16) from 1980-87 vs. 1991-97.

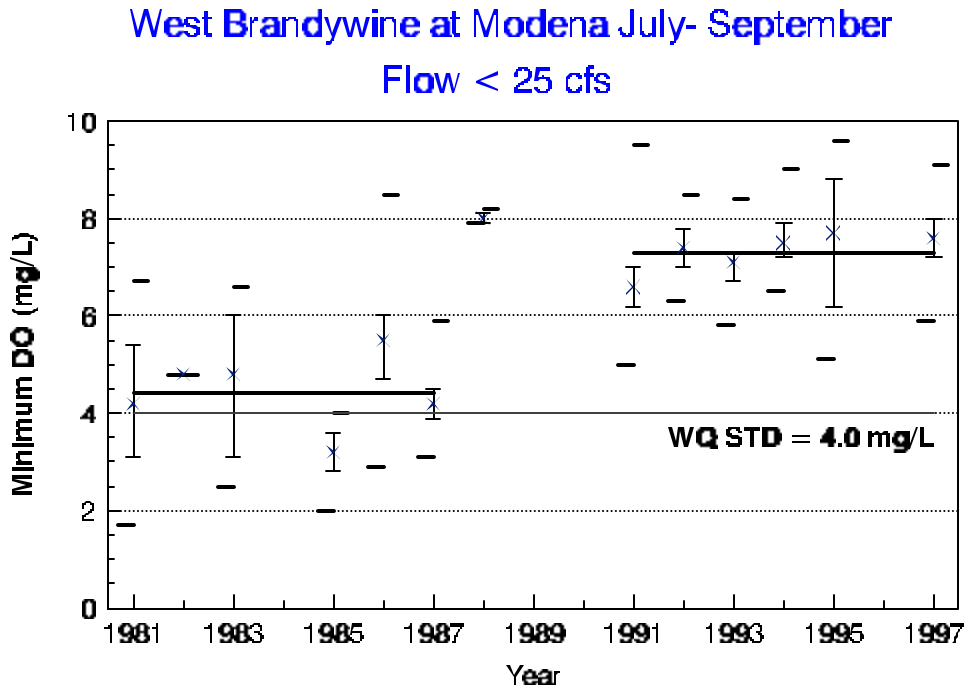

Figure 12. Box plots of minimum DO for the West Branch Brandywine at Modena for data from July-September at flows less than 25 cfs.

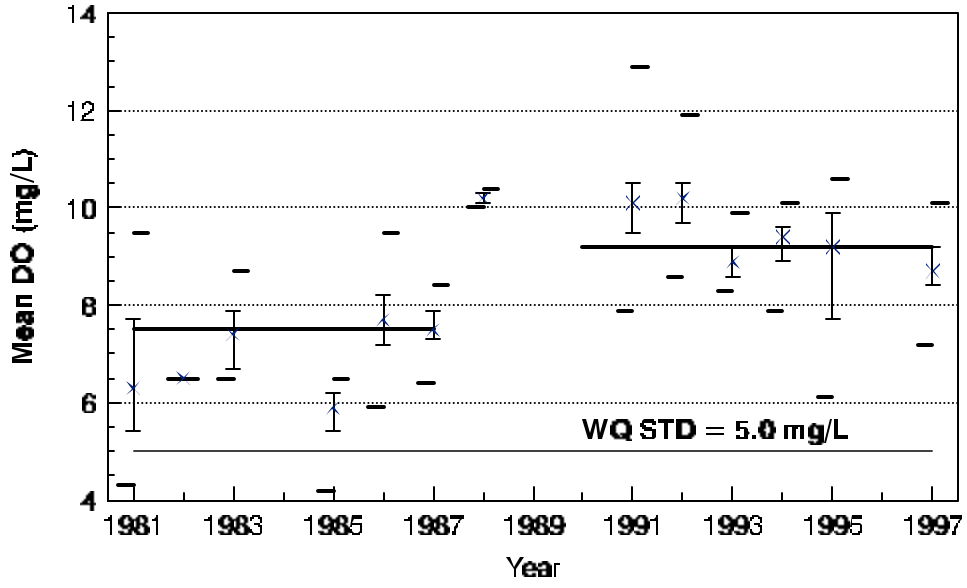

Figure 13. Box plots of mean DO for the West Branch Brandywine at Modena for data from July-September at flows less than 25 cfs.

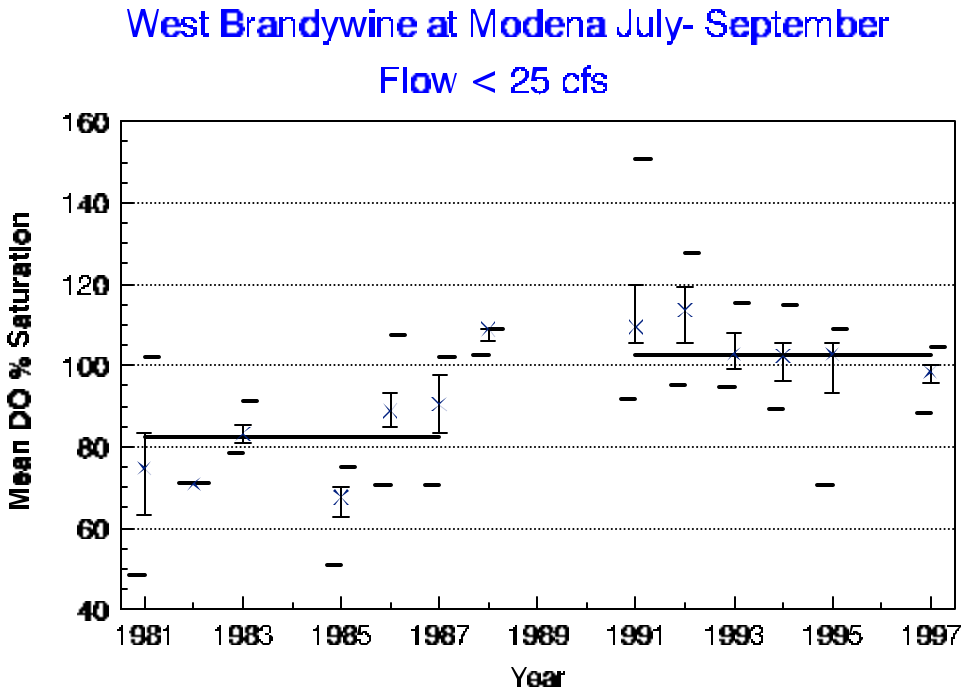

Figure 14. Box plots of mean DO % saturation for the West Branch Brandywine at Modena for data from July-September at flows less than 25 cfs.

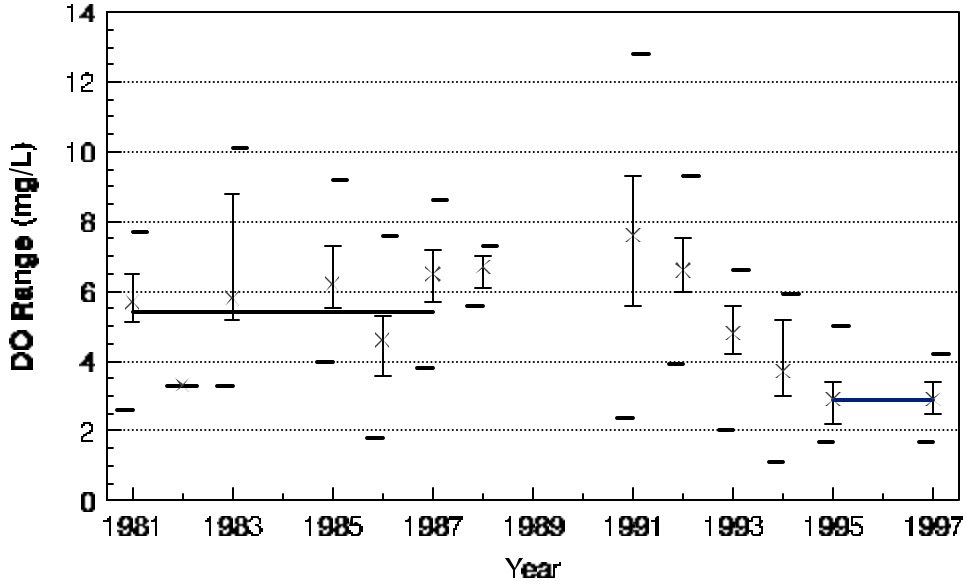

Figure 15. Box plots of daily DO range for the West Branch Brandywine at Modena for data from July-September at flows less than 25 cfs.

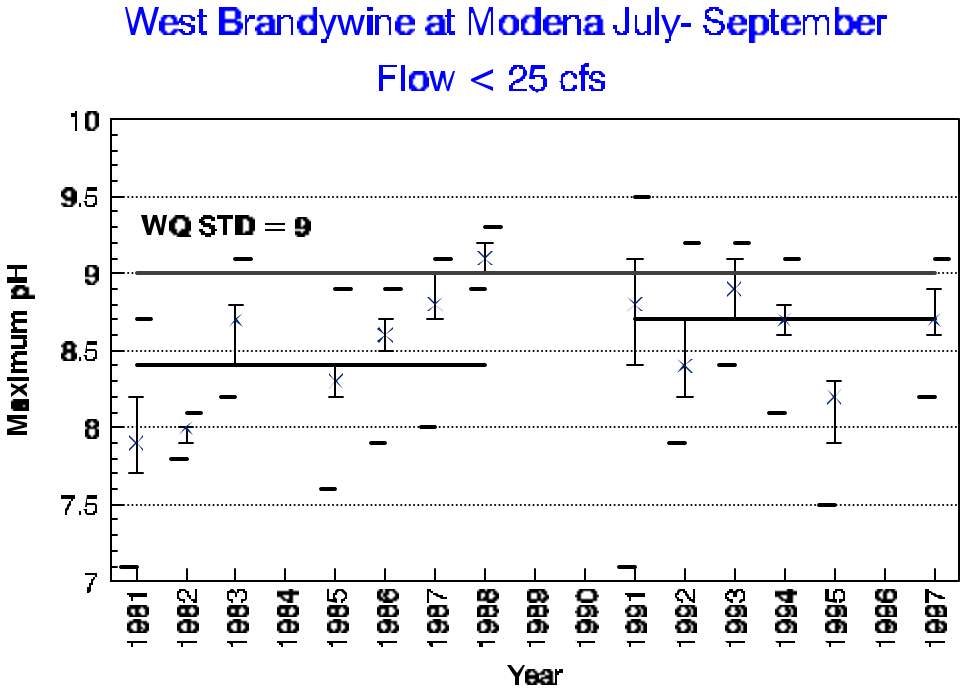

Figure 16. Box plots of maximum pH for the West Branch Brandywine at Modena for data from July-Sep

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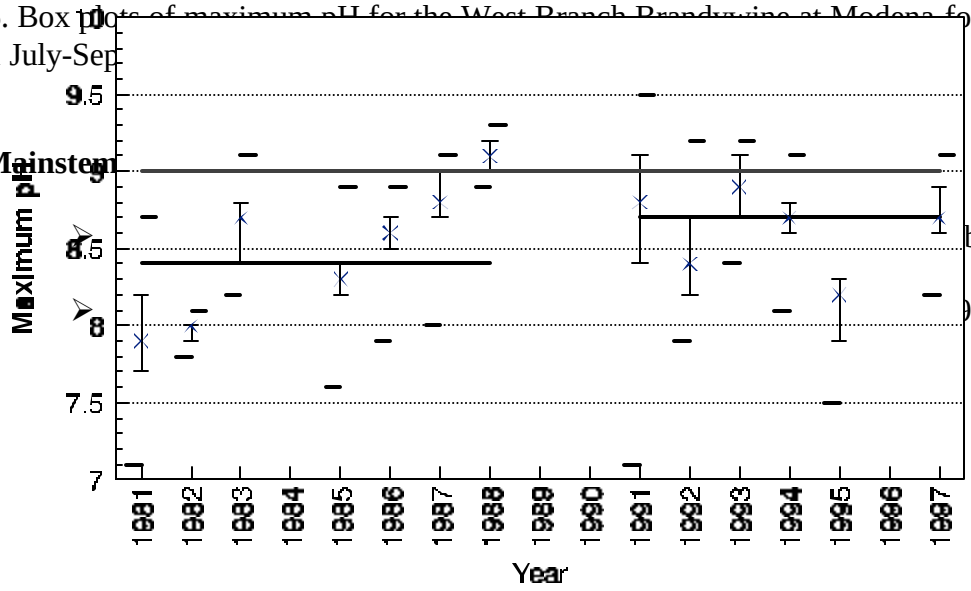


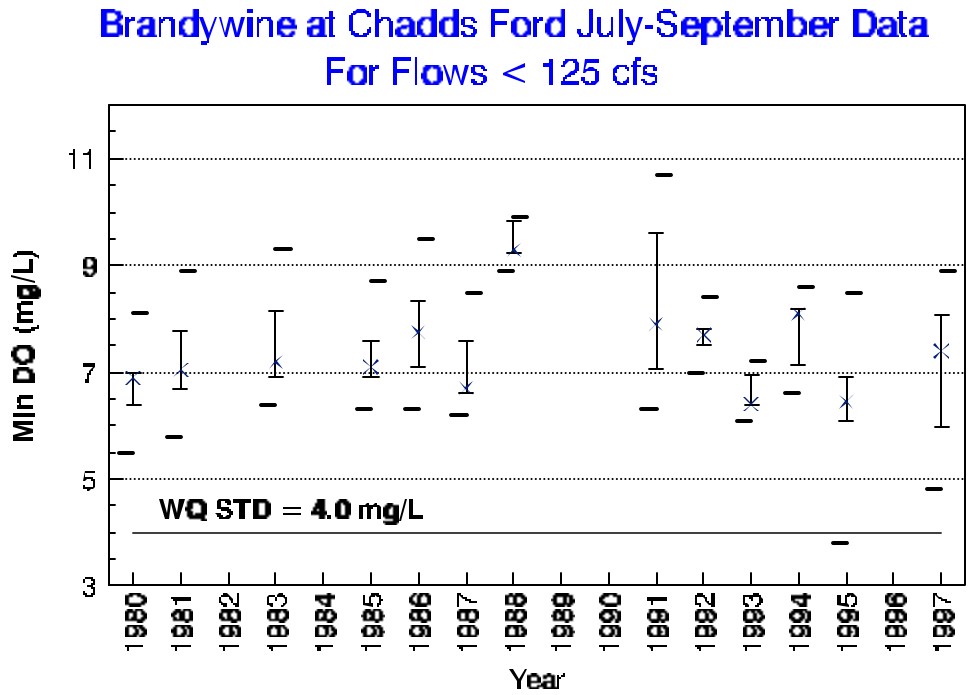


Figure 17. Box plots of minimum DO for the Brandywine at Chadds Ford for data from July-September at flows less than 125 cfs.

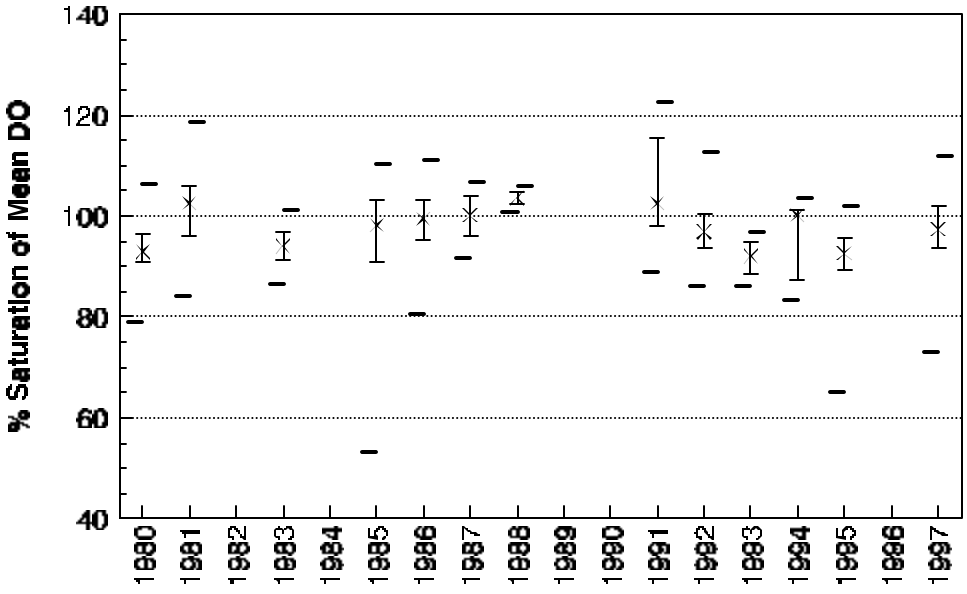


Figure 18. Box Plots of mean DO % saturation for the Brandywine at Chadds Ford for data from July-September at flows less than 125 cfs.

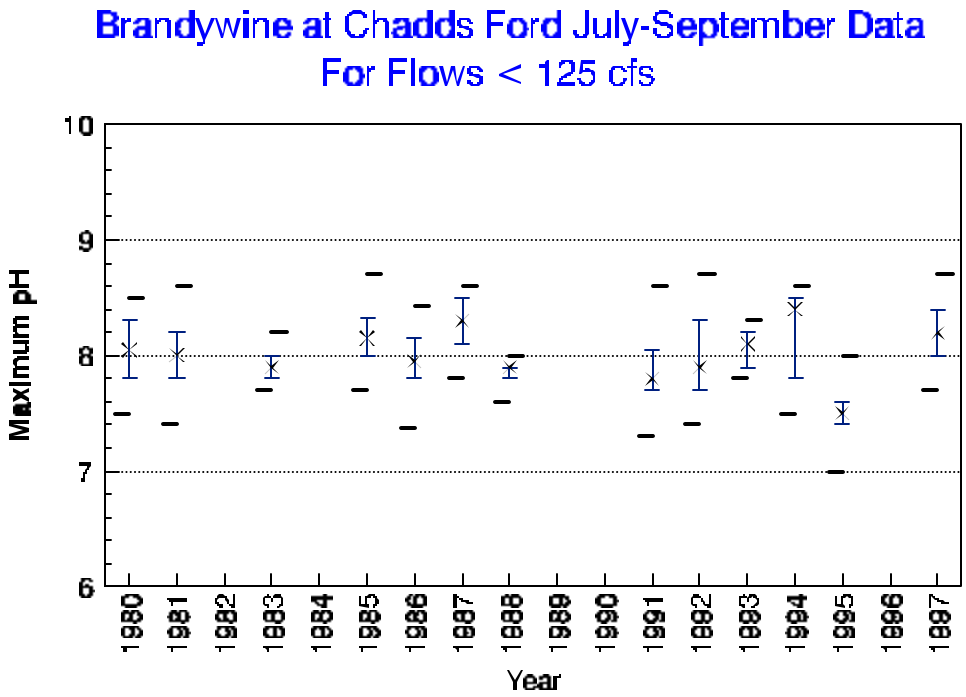


Figure 19. Box Plots of maximum pH for the Brandywine at Chadds Ford for data from July-September at flows less than 125 cfs.

Analysis of Nutrient Data for Low Flow Conditions

Methods and Procedures:

Nutrient data for the Brandywine River were analyzed to describe existing conditions (concentration and mass load) and identify changes in water quality under low-flow conditions from 1980-1997. Nutrient concentration data, including nitrite+nitrate nitrogen, ammonia nitrogen, total phosphorus and soluble ortho-phosphorus, were obtained from USGS, PA DEP, and DE DNREC databases. Flow data were obtained from USGS flow gaging stations, and the water quality and flow data were combined. Mass loads for each nutrient were calculated by multiplying the daily flow rates by the nutrient concentration data.

Since the stations on the East and West Branches at Wawaset did not have a continuous record of flow data, daily flow rates for these stations were estimated based on flow rates recorded at the next upstream stations. A relationship was derived for low flow conditions by regression of the Q1-10, Q7-10, and Q30-10 design flows reported for each station (as reported by the USGS Low-Flow Statistics report for the Christina Basin). The regression equations were then used to estimate daily flow rates at the Wawaset stations.

The flow data were first analyzed to determine an acceptable criterion for low flow conditions. The 20^{th} percentile flow (80% of flows were greater) from the entire database (1980-1997) was selected as a trial flow, which corresponded to approximately the 50^{th} percentile flow for the July-September period (see cumulative frequency distributions in

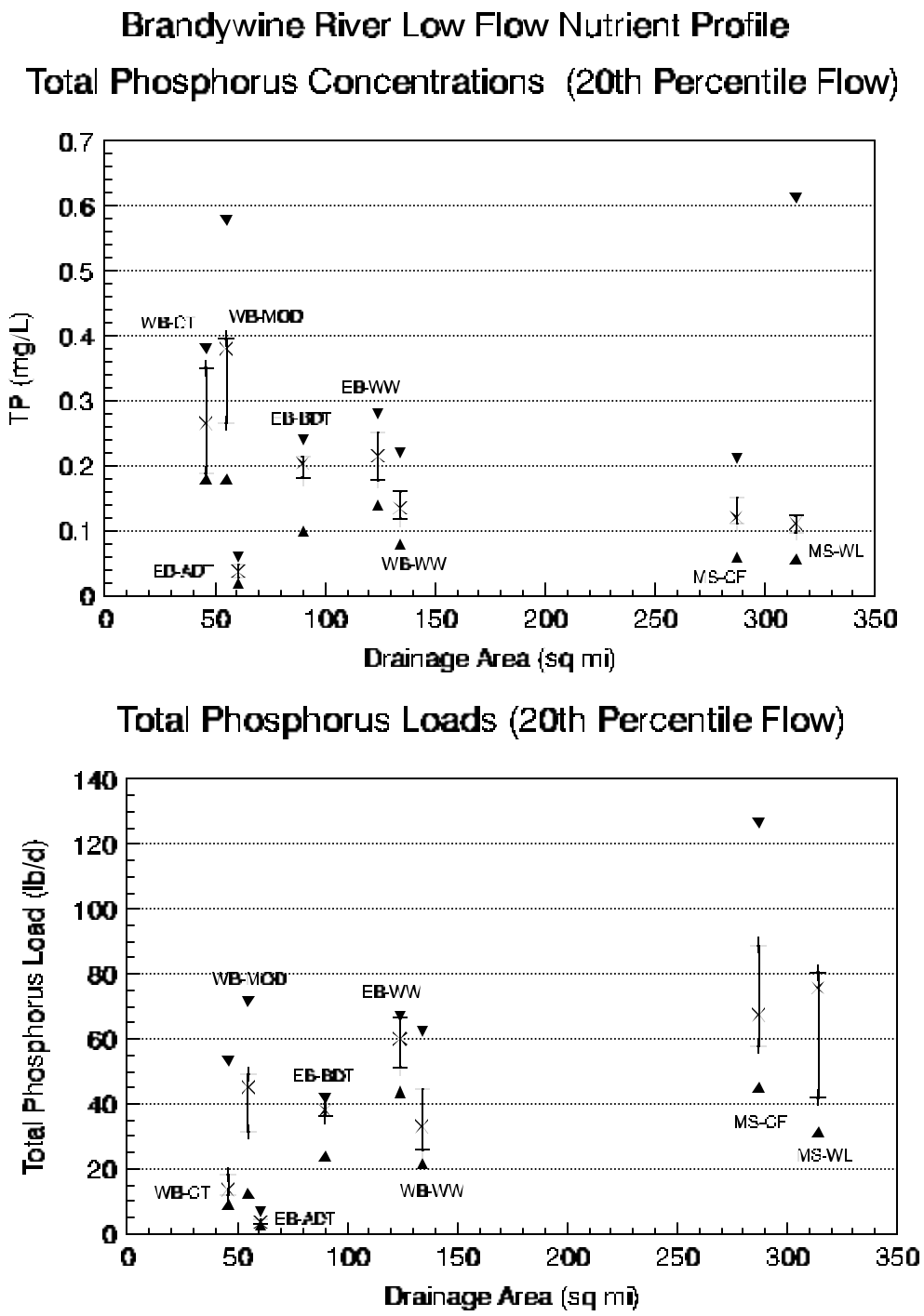
Appendix A). This criterion was also found to provide sufficient water quality data for examining current conditions and changes in water quality over time.

The selected low-flow water quality data was analyzed for seasonal trends. Most of the low-flow data were collected during July-October, with some data from June and November. The June-November data was included in these analyses unless there was some reason to exclude it, such as seasonal changes in treatment requirements. The selected nutrient concentrations and mass loads were plotted versus time to identify any changes. If changes were apparent over time, the data from each time period were summarized and the medians were compared using the Mann-Whitney test to quantify statistically significant changes at the 0.05 level of significance. If no changes were apparent, the current water quality conditions were described for the last five years of data (1993-1997). Only the most recent data were described if changes were apparent within the last five years, or if less than five years of data existed. The median, upper and lower quartile, maximum, and minimum values were derived for each station.

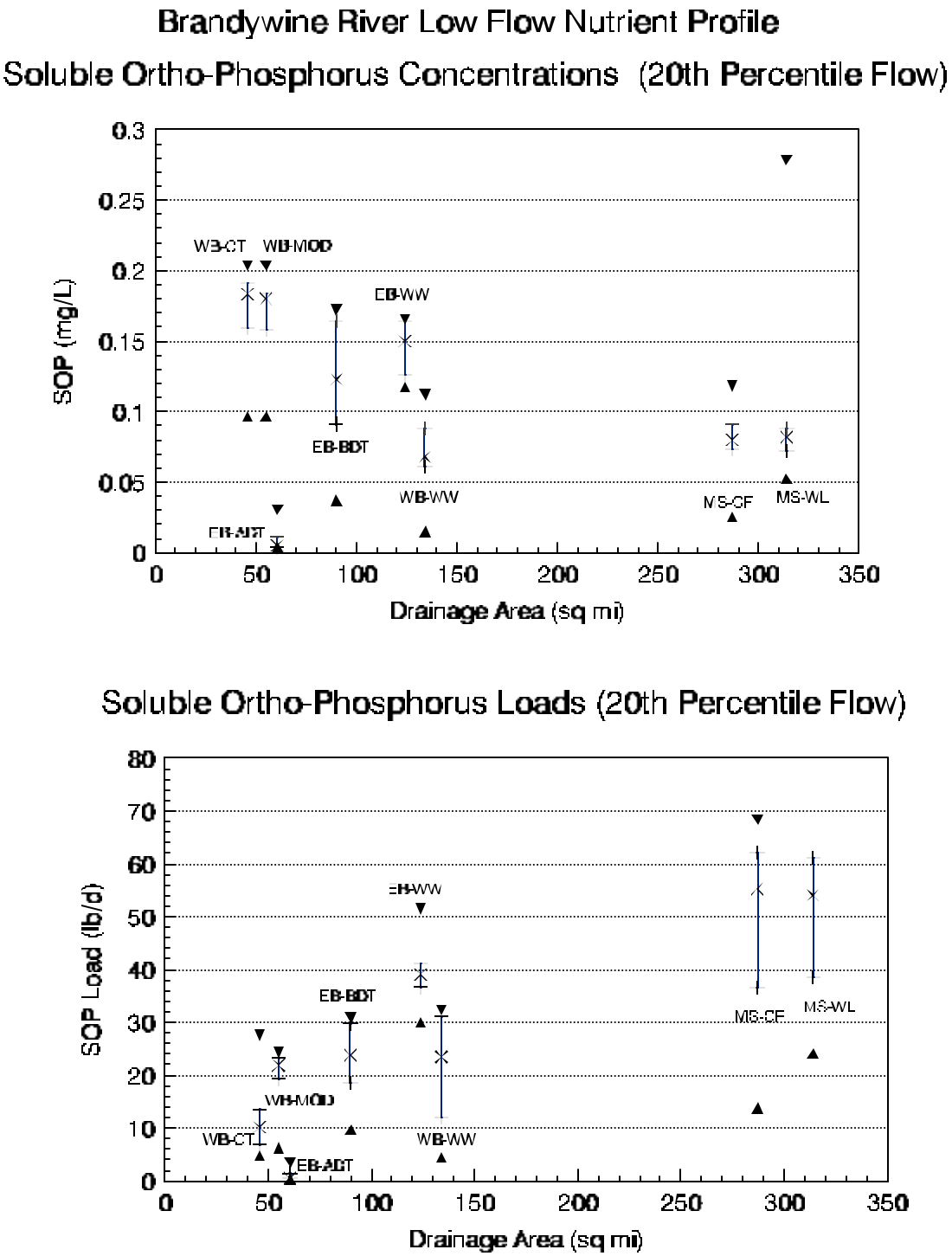
Results:

Appendix B contains the time series graphs of nutrient concentrations (NH_3-N, NO_2 + NO_3 – N, Tot. P, and SOP) at each station. Two graphs are presented for each nutrient: the first graph shows the plots of nutrient concentration and flow rate versus time for all the data; the second graph shows the nutrient concentrations and mass loads for low-flow conditions. Figures 20-23 show box plots of nutrient concentration and mass loads versus

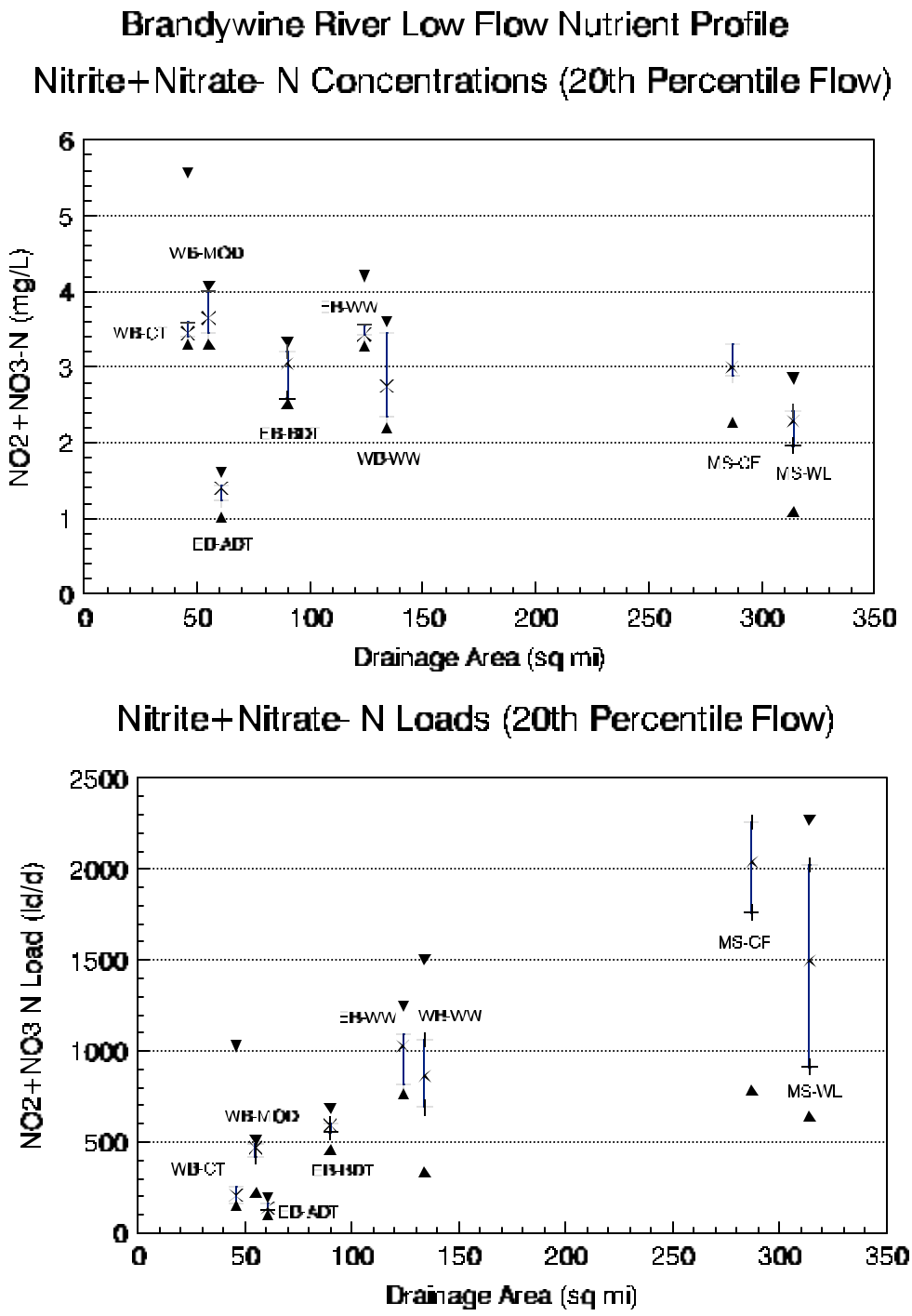
drainage area for the stations analyzed on the Brandywine River. The data in these graphs represent the most recent data, generally from 1993-1997 (Appendix C contains a tabular summary of this data). Table 5 summarizes the median nutrient concentrations and mass loads at each station for each period of data. Values preceded by '**' indicate a statistically significant (0.05 level of significance) change from the earlier data as determined by the Mann Whitney test. The findings of these analyses are discussed below by river segment (East Branch Brandywine, West Branch Brandywine, and Mainstem Brandywine).



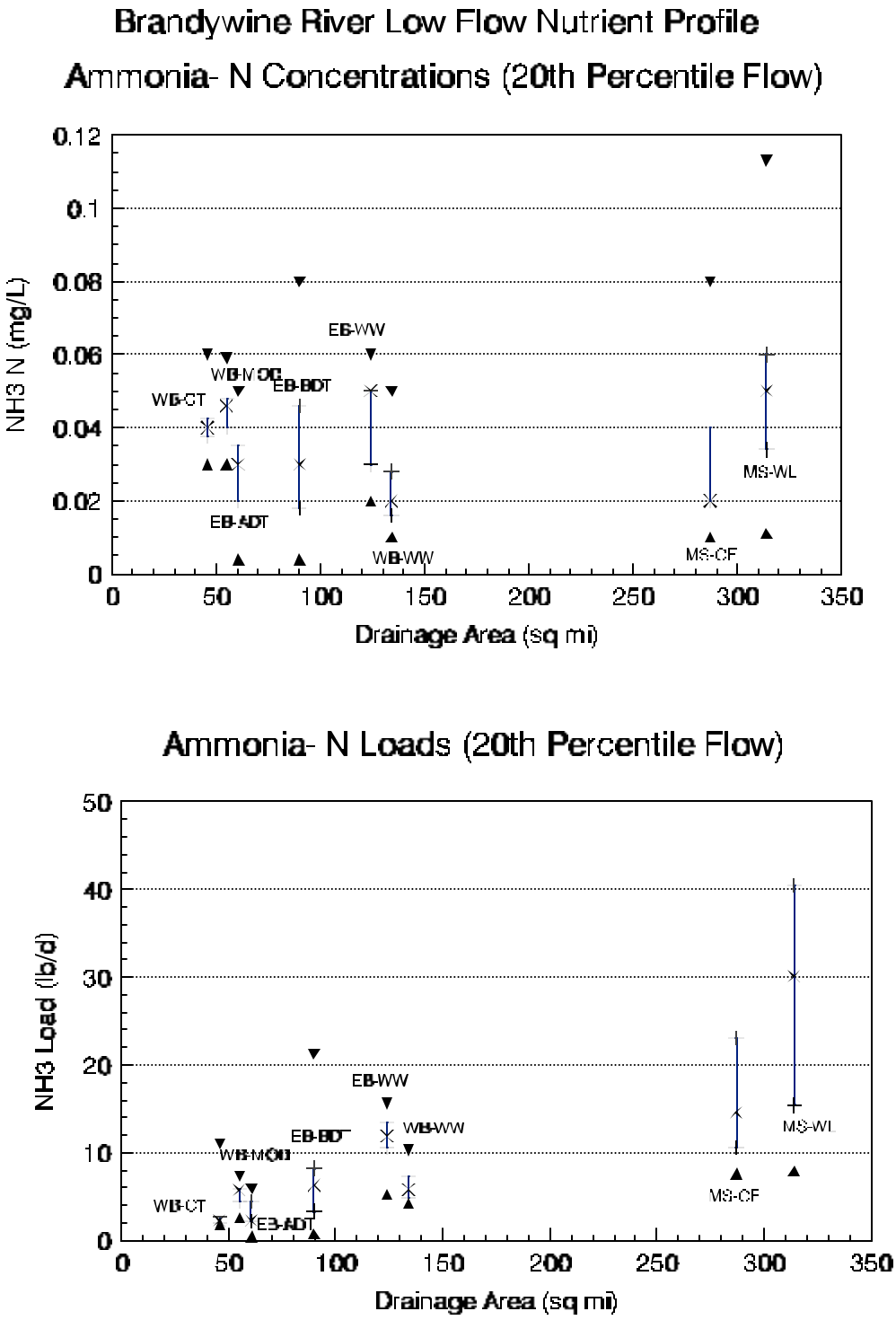
Figures 20a and b. Box plots of total phosphorus concentration and mass load versus drainage area for the Brandywine River. EB = East Branch, WB = West Branch, MS = Mainstem, CT= Coatesville, ADT= above Downingtown, BDT = below Downingtown, MOD= Modena, CF= Chadds Ford, and WL = Wilmington.



Figures 21a and b. Box plots of soluble ortho- phosphorus concentration and mass load versus drainage area for the Brandywine River. EB = East Branch, WB = West Branch, MS = Mainstem, CT= Coatesville, ADT= above Downingtown, BDT = below Downingtown, MOD= Modena, CF= Chadds Ford, and WL = Wilmington.



Figures 22a and b. Box plots of nitrite + nitrate-nitrogen concentration and mass load versus drainage area for the Brandywine River. EB = East Branch, WB = West Branch, MS = Mainstem, CT= Coatesville, ADT= above Downingtown, BDT = below Downingtown, MOD= Modena, CF= Chadds Ford, and WL = Wilmington.



Figures 23a and b. Box plots of ammonia-nitrogen concentration and mass load versus drainage area for the Brandywine River. EB = East Branch, WB = West Branch, MS = Mainstem, CT= Coatesville, ADT= above Downingtown, BDT = below Downingtown, MOD= Modena, CF= Chadds Ford, and WL = Wilmington.

Table 5. Summary of median nutrient concentrations and mass loads for the Brandywine River.

Station	Period	TP mg/L	TP Load lb/d	SOP mg/L	SOP Load lb/d	NH3-N mg/L	NH3-N Load lb/d	NO3-N mg/L	NO3-N Load lb/d
Above Downingtown	81-92	0.01	1.7	No Data	No Data	0.08	12.9	1.65	267
	95-97	** 0.04	3.5	0.005	0.6	** 0.03	** 2.3	1.40	** 138
Below Downingtown	95-97	0.20	38.1	0.123	23.8	0.03	6.3	3.05	592
Wawaset-East Branch	80-88	0.71	253.0	0.650	201.5	0.06	21.9	2.60	760
	94-97	** 0.21	** 60.0	** 0.150	** 39.1	0.05	11.9	** 3.40	1027
Coatesville	95-97	0.27	13.5	0.184	10.2	0.04	2.3	3.45	205
Modena	80-87	0.19	24.8	No Data	No Data	0.07	7.5	2.61	325
	95-97	0.38	45.1	0.180	21.9	0.05	5.7	** 3.65	469
Wawaset West Branch	80-88	0.18	61.0	0.130	51.3	0.01	4.0	3.10	898
	92-97	0.14	33.1	** 0.067	** 23.5	0.02	5.9	2.74	865
Chadds Ford	80-87	0.37	248.8	0.290	216.4	0.05	32.9	2.30	1589
	92-97	** 0.12	** 67.4	** 0.080	** 55.3	** 0.02	** 14.6	** 3.00	** 2041
Wilmington	80-87	0.26	177.5	No Data	No Data	0.01	79.8	1.97	1315
	92-97	** 0.11	** 72.9	0.082	54	0.05	34.6	2.22	1479

East Branch Brandywine

The station above Downingtown has lowest nitrate-nitrogen and phosphorus concentrations of all the stations examined for the Brandywine River. For the 1995-97 data, total phosphorus concentrations increased while ammonia-nitrogen concentrations and loads decreased. There was no statistically significant change in nitrate-nitrogen concentrations, however nitrate mass loads decreased.

Nutrient concentrations and loads in the East Branch Brandywine increase as the river flows through Downingtown to Wawaset as indicated in Figures 20-23. The data collected at Wawaset on the East Branch Brandywine River indicates that significant reductions in phosphorus concentrations and mass loads occurred between 1988 and 1993, however nitrate concentrations increased between these time periods.

West Branch Brandywine

The upper station (Coatesville) on this branch has significantly higher phosphorus and nitrogen loads than the comparable station on the East Branch Brandywine. The data collected at the Modena station below Coatesville indicates that only the nitrate concentrations increased significantly from the 1980's. The current nutrient concentrations at Modena are similar to the values measured for the station at Coatesville. The data at Wawaset on the West Branch indicates a significant reduction in soluble ortho-phosphorus concentrations occurred between 1988 and 1992. In general, the nutrient concentrations at Wawaset on the West Branch are lower than the concentrations measured at Modena, and are also lower than those measured at Wawaset on the East Branch Brandywine.

Mainstem Brandywine

The nutrient concentrations at Chadds Ford were generally between the concentrations noted for the Wawaset stations on the East and West Branches. Phosphorus concentrations and mass loads decreased at this station between 1988 and 1992, which may be related to the decrease in phosphorus noted on the East Branch Brandywine. The nitrate-nitrogen concentrations increased between 1988 and 1992 similar to the increase in nitrate concentrations on the East Branch at Wawaset.

The nutrient concentrations and mass loads at the Wilmington station were very similar to those measured at Chadds Ford. The nitrate concentrations and mass loads

were actually less than measured at the Chadds Ford station. There was a significant decrease in phosphorus concentrations at the Wilmington station between 1988 and 1992.

Summary of Findings for the Brandywine River

The major findings of the data analysis for low flow conditions on the Brandywine River are summarized below.

- Dissolved oxygen concentrations at the stations below Downingtown on the East Branch and at Modena on the West Branch increased significantly after 1987. Prior to 1987, frequent violations of dissolved oxygen criteria were noted, however, no DO criteria violations have been detected since 1987.

- Maximum daily pH values have increased at the stations below Downingtown on the East Branch and at Modena on the West Branch since 1987. Frequent violations of the maximum pH criteria (pH=9) have been recorded at each station. The high pH values may be related to the uptake of carbon dioxide and nutrients algae and plants during photosynthesis.

- The DO and pH concentrations at the Chadds Ford station on the mainstem Brandywine have not changed significantly since 1980. Although the DO data were generally in compliance with the DO criteria for the July-September data, there were occasional excursions of the maximum pH criteria of 8.5 over the period from 1980-1997.

- Phosphorus concentrations and mass loads have decreased significantly since 1988 at the East Branch below Downingtown, West Branch below Modena, and the mainstem at Chadds Ford and Wilmington. However, nitrate-nitrogen concentrations and mass loads have increased since 1988 at the stations below Downingtown on the East Branch and at Chadds Ford on the mainstem.

- In terms of spatial trends in nutrient concentrations and mass loads, phosphorus and nitrogen levels increase along the East Branch, starting at relatively low levels above Downingtown and increasing through the station at Wawaset. Nitrogen and phosphorus concentrations and mass loads for the West Branch reach a peak at the Modena station and decrease moving downstrean to the station at Wawaset. The East Branch generally delivers higher nutrient concentrations and loads to the mainstem than the West Branch.

- The phosphorus loads at the Chadds Ford station on the mainstem appear to be slightly less than the sum of the mass loads for phosphorus from the East and West Branches. The nitrate nitrogen mass loads at Chadds Ford were slightly higher than the sum of the mass loads from the East and West Branch.

- The phosphorus mass loads at the Wilmington station on the mainstem Brandywine were not significantly different from the loads measured at Chadds Ford. Nitrate-nitrogen mass loads were less at Wilmington than at Chadds Ford.